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PLASMON ASSISTED SYNTHESIS OF HIGHLY FLUORESCING SILVER QUANTUM CLUSTER / POLYMER COMPOSITES FOR BIOCHEMICAL SENSING

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Plasmonics is combined with polymer synthesis for rapid fabrication of highly fluorescing silver quantum cluster / polymer composites inside microfluidic channels. UV-light assisted synthesis of polymers has been investigated by a number of groups previously [1], however, plasmon assisted synthesis has not been presented before. This should allow highly localized fabrication of porous polymers that are defined by the location of the nanoplasmonic metal film.
Silver quantum clusters (AgQCs) consisting of 2-10 atoms can be highly fluorescing in the visible wavelength range and possess a much greater photostability than organic fluorophores [2]. In this work AgQCs are embedded into the oligoaniline porous matrix and is employed for indirect fluorescence detection of cyanide in a simple microfluidic.

The reaction mechanism is based on the well-known oxidative polymerization of aniline and pyrrole [1], where silver cations (by addition of $AgNO_3$ to the solution) can be used as a reducing agent. In this work, no $AgNO_3$ is added, but was generated locally by plasmon-assisted photochemical oxidation of AgNPs. It is known that AgNPs slowly oxidize in aqueous solution, thereby releasing Ag+, however, with a half-life of several days [3]. It was found that by excitation of the plasmon resonance band, the oxidation (Ag-cation release) was enhanced dramatically. Aniline/pyrrole reduce Ag+ back to fluorescing AgQCs at the surface of the AgNPs, while undergoing oxidative polymerization. Hence, the polymer/oligomer grows from the AgNP film, while AgQCs are being embedded into the matrix. This can happen at a time scale of second and during photoactivation, the fluorescent signal emanating from AgQCs increases rapidly with time.

The fluorescing composite was tested for detection of cyanide. Here, so-called nucleophile activated oxidative dissolution was employed for destruction of the AgQCs [3]. The nucleophile (cyanide) donates an electron pair at the AgQC surface through a coordinative bond. This increases the electron density at the surface, thereby displacing free electron density towards the bulk. This results in a decreased reduction potential, thereby promoting oxidation by dissolved oxygen in solution [4].

Overall, we strongly believe that plasmon assisted polymer synthesis will receive great interest for localized fabrication of porous polymers inside fluidic channels, with possibly sub-micrometer resolution, as well as for development of new types of fluorescence sensors.

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